Bio-Recovery of Silver from Simulated Silver Electroplating Wastewater Using Palm (*Elaeis guineensis*) Leaves Extract

Ahmad Arif
Junaidah Jai
Norashikin Ahmad Zamanhuri
Faculty of Chemical Engineering, Universiti Teknologi MARA (UiTM), 40450 Shah Alam, Malaysia

ABSTRACT

In this research, the role of an eco-friendly biomaterial, palm (Elaeis guineensis) leaves extract as a reducing and stabilizing agent to recover precious metal silver from simulated silver electroplating wastewater, was studied. The phytochemical compounds present in the palm leaves extract, which possesses antioxidant properties, were characterized according to their functional groups and the parameters involved in affecting the silver bio-recovery effectiveness were investigated. The studies found that major types of phytochemical compounds that assist silver bio-recovery were polyphenols, alcohols, carboxylic acid and reducing sugars. Meanwhile, the parameters of reactant's concentration ratio, acidity and metal impurities were found to absolutely affect the silver bio-recovery effectiveness. The characterization of the recovered suspended solid particles after the bio-reduction process reveals that silver metals with high degree of crystallinity were successfully recovered and in nano-sized.

Keywords: *Palm Leaves Extract, Natural Antioxidant, Silver Wastewater, Bio-Recovery, Silver Nanoparticles.*

Introduction

Electroplating is the application of a metal coating onto a metallic or other conducting surfaces by an electrochemical process [1]. This process however could generate a lot of metal wastes mainly in rinsewater and spent electroplating bath solution [2]. For common metals, it is still acceptable to

ISSN 1823-5514, eISSN 2550-164X

Received for review: 2016-12-07
Accepted for publication: 2017-01-20
Published: 2017-05-15

discard the waste directly to the local waste management authority. However, in precious metal electroplating, expensive price of the metals such as gold, silver and palladium have attracted lots of interests to recover this type of metals from the waste [3]. Hence, a suitable wastewater treatment is required not only to remove the metals but also to recover those precious metals. Recently, several conventional wastewater treatment methods have been applied to recover these precious metals such as chemical precipitation, ion exchange, coagulation and flocculation, adsorption, membrane filtration, flotation, electrochemical treatment and photocatalysis [4], [5]. Every method has its own advantages and disadvantages in practical applications; however, the operational cost and effectiveness are the main issue in selecting which method is the best.

In typical silver electroplating industry, silver cyanide baths are widely used since it offers the most consistent mirror bright, compact and smooth silver deposit qualities at the lowest cost [6], [7]. In addition, according to ASTM standard specification for electrodeposited coatings of silver for engineering use [8], articles that need to be coated must undergo copper undercoating first that is plating a thin layer of copper on the articles surfaces which later will act as an adhesive for silver plating. Hence, the rinsewater from silver electroplating production line will also contain copper (II) ions and some trace of miscellaneous metal cations [9].

Bio-recovery methods which utilize plant parts or living microorganisms to recover precious metals from wastewater are being increasingly explored recently by several researches concerning on green technology applications [10]–[13]. One of it is bio-reduction using plants (inactivated plant tissue, living plant and plant extract). Extracts from several plants are known to contain a naturally occurring phytochemicals which exhibit great antioxidant properties [14]. This oxygen-containing free-radicals bioactive compounds have the abilities to act as both reducing and stabilizing agents which is first to reduce the metal ions to metal solid and then to stabilize the colloidal metal solid formed in the solutions [15], [16].

Oil palm (*Elaeis guineensis*) trees are cultivated widely in Malaysia to support the vast growth of palm oil industries. During the harvesting process, palm leaves are pruned and left decomposed. According to Arham *et al.* [16], palm leaves extract contains polyphenolic compounds which are capable to act as reducing agent for reduction reaction in nanoparticle synthesis. Hence, we believe that palm leaves extract can be used to recover silver from silver containing wastewater by bio-reduction process. However, the physical and chemical characteristics of wastewater vary amongst industries. Therefore, this present study will investigate the effect of palm leaves extract ratio, silver ions concentration, acidity and impurities on silver recovery effectiveness.

Methodology

Preparation of palm leaves extract

Fresh palm leaves were collected, washed with distilled water, cut into small pieces and oven dried at 70°C for 12 hours. The dried palm leaves were then grinded into powder using grinder. 500 mL of distilled water was heated in a beaker until it reached temperature 70°C. 50 g of the palm leaves powder were weighted and poured into the beaker. The mixture was stirred for 10 minutes and filtered using filter paper. The palm leaves extract obtained was stored in refrigerator at 4°C [17].

Preparation of simulated silver electroplating wastewater

According to Su *et al.* [5], typical concentration of silver (I) ions in wastewater generated from metal surface cleaning and rinsing process is between 1000 to 3000 mg L^{-1}. However, because of the toxicity of cyanide which could pose extremely high risks to human health and the environment, silver nitrate is used in this experiment instead of silver cyanide with the same silver ions concentration.

Characterization of palm leaves extract

First, the palm leaves extract was dried using freeze dryer. Then, 2g of the dried palm leaves extract was dissolved in 100 mL of methanol and analysed in gas chromatography–mass spectrometry (GC-MS).

The GC-MS analysis was done on a thermo gas chromatograph coupled to ion-trap mass spectrometer (model Varian 450-GC 240-MS) equipped with VF-624 capillary column (30 m long, 0.25 mm i.d., film thickness 1.4 μm). The column temperature program was 50°C for 6 min, with 5°C increases per min to 250°C; which was maintained for 30 min. The carrier gas was helium at a flow rate of 1 mL/min (splitless mode). The detector and injector temperatures were both maintained at 250°C. The quadrupole mass spectrometer was scanned over the range 28–400 amu at 1 scan s^{-1}, with an ionizing voltage of 70 eV, an ionization current of 150 Ma and an ion source temperature of 200°C. To determine the Kovats index of the components, a mixture of alkenes (C9–C24) was added to the crude extract before injecting it in the GC–MS equipment and analyzed under the same conditions as above [18]. The compounds were identified by computer searches in commercial libraries of NIST (National Institute of Standard and Technology) and by their Kovats retention indexes.

Silver bio-recovery

Factor 1: Reactant's concentration ratio

Thirty ml of palm leaves extract was added into 70 ml of 500 ppm silver (I) ions solution (silver nitrate solution) and stirred for 2 hours. Then, the mixture was centrifuged at 14000 rpm for 10 minutes and the unreacted silver ions concentration was measured using atomic absorption spectroscopy, AAS (model Hitachi Z-2000). The sedimented suspended solids were recovered and oven dried at 70°C for 12 hours. To study the effect of reactant's concentration ratio, the experiments were repeated at different silver ions concentrations of 1000 ppm, 1500 ppm, 2000 ppm, 2500 ppm and 3000 ppm.

Factor 2: Wastewater acidity

Thirty ml of palm leaves extract was added into 70 ml of 500 ppm silver (I) ions solution (silver nitrate solution) at pH 5 and stirred for 2 hours. Then, the mixture was centrifuged at 14000 rpm for 10 minutes and the unreacted silver ions concentration was measured using AAS. The sedimented suspended solids were recovered and oven dried at 70°C for 12 hours. To study the effect of acidity, the experiments were repeated at different pH of 0, 1, 2, 3 and 4. The acidity of the silver nitrate solution was adjusted by adding 0.1M nitric acid.

Factor 3: Metal Impurities

Thirty ml of palm leaves extract was added into 70 ml of 10% impurities mixture of 500 ppm silver (I) ions (silver nitrate) and 50 ppm copper (II) ions (copper nitrate) solution and stirred for 2 hours. Then, the mixture was centrifuged at 14000 rpm for 10 minutes and the unreacted silver ions concentration was measured using AAS. The sedimented suspended solids were recovered and oven dried at 70°C for 12 hours. To study the effect of metal ions impurities, the experiments were repeated at different impurities of 20%, 30%, 40% and 50% copper (II) ions.

Characterization of the bio-recovered solid particles

The bio-recovered solid particles were characterized using field emission scanning electron microscopy, FESEM (JOEL JSM-6360A) equipped with X-ray energy dispersive spectrometer (EDX). The crystalline structure of the solid particles was identified through X-ray diffraction, XRD (Rigaku Ultima IV powder diffractometer) using Cu Kα radiation (λ = 1.54056 Å) operating at a voltage of 40 kV and a current of 40 mA between 10˚ to 80˚ at the scanning rate of 2˚ per minute [19].

Result and Discussions

Characterization of palm leaves extract

From the generated GC-MS chromatogram as in Figure 1, nine peaks were chosen where each peak at a retention time may represent one or more compounds that possess antioxidant activity present in the palm leaves extract (Table 1). Retention time is the time between sample injection and appearance of a solute peak or known as the amount of time that a compound is retained in the GC column.

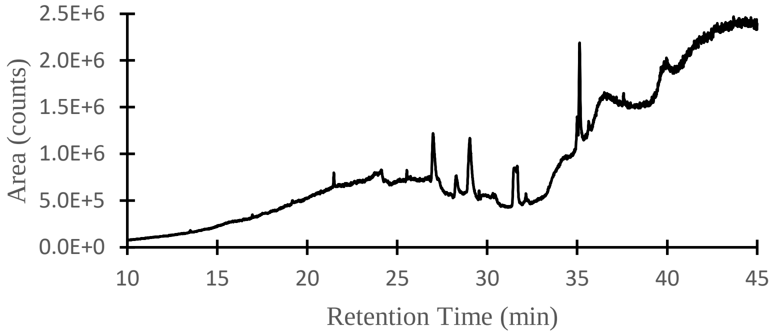


Figure 1: GC–MS chromatogram of palm leaves extract

Table 1: Chosen peaks and their respective representing major compounds

Peaks	Retention time (min)	Major compounds
1	19.3243	2-Phenyl-3-butyn-2-ol
2	21.4626	1,2-Benzenediol, 3,5-bis (1,1-dimethylethyl)
3	26.9900	Thymol
4	28.2803	Phytol
5	29.0141	3,5-Dihydroxytoluene
6	29.5436	d-Mannose
7	29.5517	Tetradecanoic acid
8	34.9927	Hyodeoxycholic acid
9	35.1275	Ricinoleic acid

We have classified each of the phytochemical compounds that contains hydroxyl and carboxyl groups into four major classes namely polyphenols, alcohols, carboxylic acids and reducing sugars as in Figure 2.

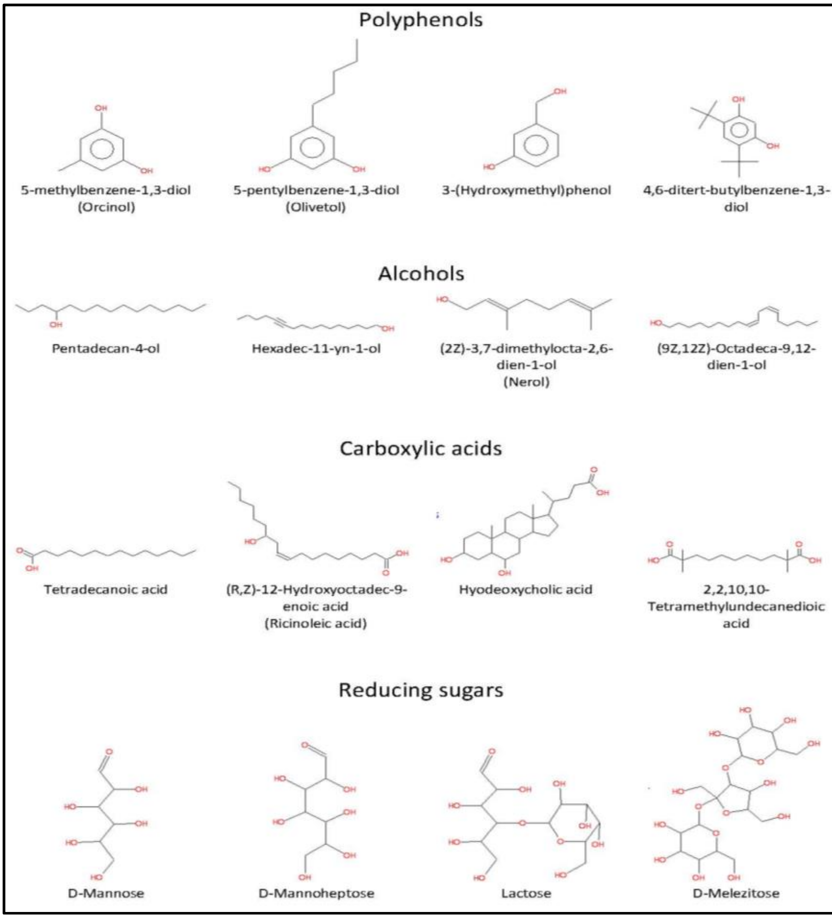


Figure 2: IUPAC name and structure of some major phytochemical bioactive compounds present in palm leaves extract

Silver bio-recovery effectiveness

The silver bio-recovery effectiveness is best described by the percentage of silver recovered from the solutions.

$$\text{Percentage of silver recovered (\%)} = \frac{\text{Initial silver ions concentration (ppm)} - \text{Final silver ions concentration (ppm)}}{\text{Total silver ions concentration (ppm)}} \times 100$$

The first factor that affects the silver bio-recovery effectiveness is the reactant's concentration ratio i.e. the concentration ratio between the silver ions and the bioactive compounds. According to Arham *et al*. [17], the concentration of the bioactive compounds is 8 mg GAE/g dry palm leaves and hence the concentration in the palm leaves extract is 800 ppm. Referring to Figure 3, the best optimum ratio of silver ions to bioactive compounds is 1.46 which results 99% of silver being recovered. Beyond that, the percentage of silver being recovered will reduce since the bioactive compound is the limiting reactant.

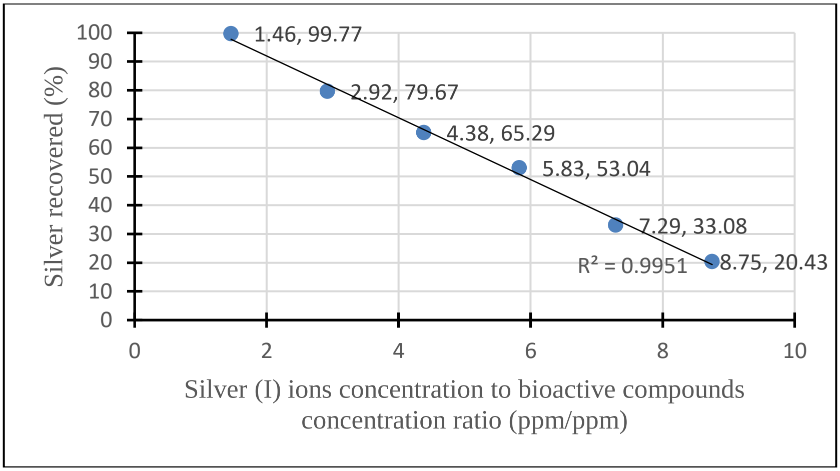


Figure 3: Effect of reactant's concentration ratio to silver bio-recovery effectiveness

The second factor that affects the silver bio-recovery effectiveness is the reaction acidity. Increasing acidity of the reaction medium will reduce the percentage of silver being recovered (Figure 4). This happens because a change in pH will result in a charge change of the bioactive compounds contained in the palm leaves extracts which later will affect their ability to react with silver ions. Makarov *et al*. [20] suggested that the chemical equation representing this bio-reduction reaction is

$$nAg^{+} + R\text{-}(OH)_{n} \rightarrow nAg + R{=}O + nH^{+} \quad (1)$$

When the hydroxyl group wants to participate in an ionic bond, a hydroxide anion, $[OH^-]$ is released to neutralize the $[Ag^+]$ cation. Hence, in acidic conditions, excess hydrogen ions, $[H^+]$ will interfere the hydroxide anion because of the electrostatic attraction between the oppositely charged ions. Hence, most accessible silver ions will involve in a smaller number of nucleation events which then leads to agglomeration of the silver atoms and results in bigger particle sizes [21], [22].

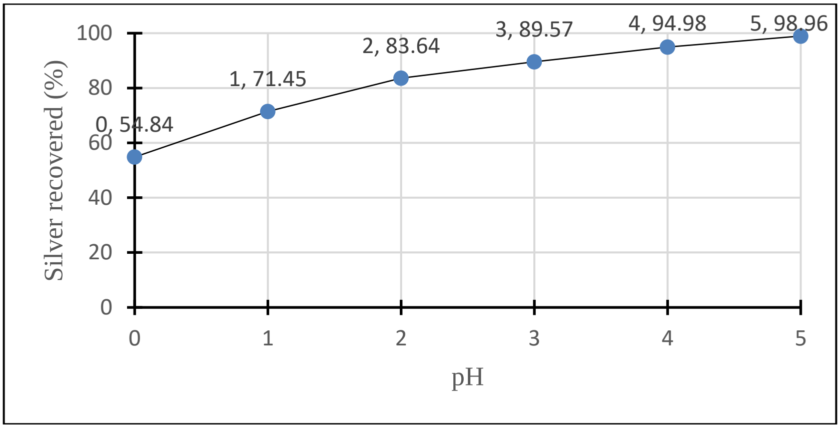


Figure 4: Effect of reaction medium acidity to silver bio-recovery effectiveness

The third factor that affects the silver bio-recovery effectiveness is the amount of other electropositive metal cations present. Although the percentage of silver being recovered drops slightly as the concentration of copper (II) ions increases, the recovery effectiveness is satisfactory [23] (Figure 5).

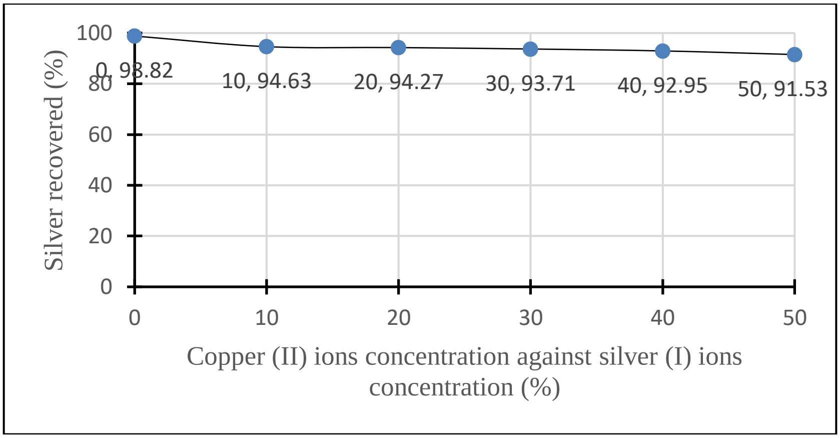


Figure 5: Effect of copper (II) ions concentration to silver bio-recovery effectiveness

Silver (I) ions is more favourable than copper (II) ions because silver is more electronegative and has higher standard reduction potentials than copper as shown in Table 2 [24], [25].

Table 2: Potentials of the Elements and Their Compounds at 25°C [26]

Elements	Symbol	Electronegativity (Pauling scale)	Half-reaction	Standard reduction potential (V)
Copper	Cu	1.90	$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$	+ 0.340
Silver	Ag	1.93	$Ag^{+}(aq) + e^- \rightarrow Ag(s)$	+ 0.799

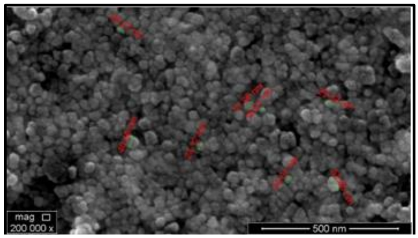
However, the percentage of silver being recovered drops because the remaining silver (I) ions has become too 'dilute' and being hindered by the 'concentrated' positively charged copper (II) ions.

Characterization of the bio-recovered solid particles

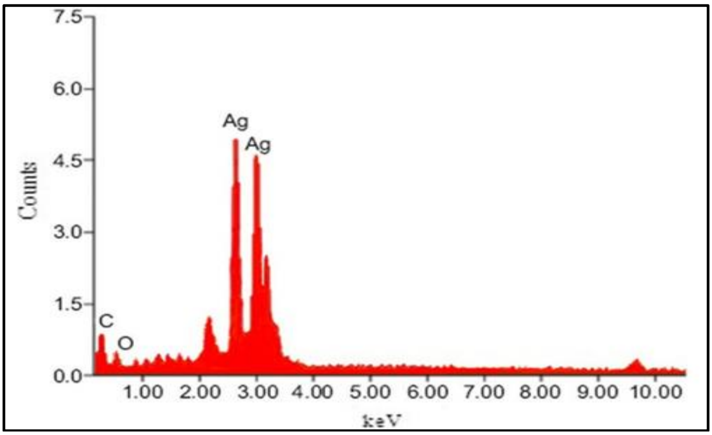
FESEM analysis of the bio-recovered solid particles revealed the morphology and size of the particles. From FESEM image in Figure 6(a), the solid particles are polydisperse and irregular spherical shape with size varying from 20 to 60 nm. Hence, it was suggested that the bio-recovered solid is in nano-sized or simply called nanoparticles.

The EDX analysis result in Figure 6(b) shows a strong signal at approximately 2.983 keV. This is a typical optical absorption peak of metallic silver nanocrystals due to surface plasmon resonance. It also observed spectral signals for carbon and oxygen which indicated that the extracellular organic moieties (from ASPE) were adsorbed on the surface or in the vicinity of the metallic silver nanoparticles [27].

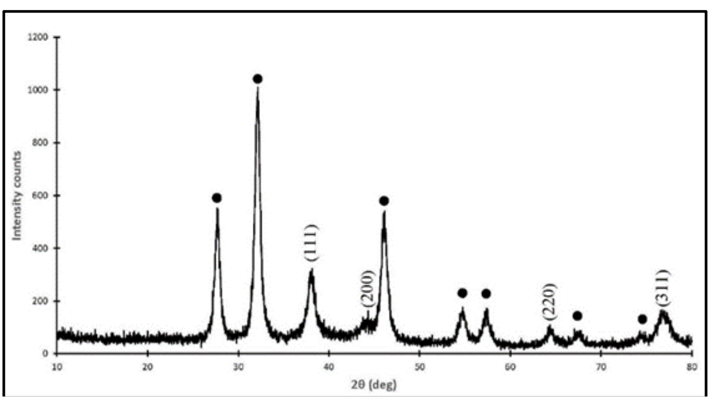
Figure 6(c) shows the XRD pattern of the bio-recovered solid silver nanoparticles. The diffraction pattern shows four sharp peaks and well defined diffraction lines at 2θ = 38.12°, 44.28°, 64.38° and 77.32° which correspond to the (111), (200), (220) and (311) Bragg reflections of face-centered-cubic (fcc) structure of metallic silver, respectively [28]. The intensity of the peaks reflects high degree of crystallinity of the bio-recovered silver nanoparticles [29]. However, the unassigned peaks noted with points reflect a crystalline bioorganic compound or metalloproteins that are naturally present in the palm leaves extract. Hence, this proved that there exists a secondary material that binds and caps silver nanoparticles in clusters [22].



(a)



(b)



(c)

Figure 6: Results of the characterized bio-recovered solid particles consists of (a) FESEM image, (b) EDX signal, and (c) XRD pattern

Conclusion

To conclude, palm leaves extract as a natural reducing and stabilizing agent can be used to recover precious metal silver from simulated silver electroplating wastewater. The phytochemical compounds present in the palm leaves extract such as polyphenols, alcohols, carboxylic acid and reducing sugars that possess great antioxidant properties were the bioactive compounds responsible in this bio-recovery process. Besides that, the parameters of reactant's concentration ratio, acidity and metal impurities were found to absolutely affect the silver bio-recovery effectiveness in their own way. The characterization of the recovered suspended solid particles after the bio-reduction process reveals that silver metals with high degree of crystallinity were successfully recovered and in nano-sized particles ranging from 20 to 60 nm. Hence, by this research, we have validated the use of palm leaves extract not just to recover silver from waste but also synthesize silver nanoparticles as the products.

Acknowledgement

The authors would like to acknowledge the Ministry of Education for Research Acculturation Grant Scheme (RAGS) Project number RAGS/2012/UITM/TK05/6 for the financial support to carry out this research.

References

[1] H. Kanematsu and D. M. Barry, *Corrosion Control and Surface Finishing: Environmentally Friendly Approaches*. Springer Japan, 2016.

[2] N. F. M. Noah, N. Othman, and N. Jusoh, "Highly selective transport of palladium from electroplating wastewater using emulsion liquid membrane process," *J. Taiwan Inst. Chem. Eng.*, 2016.

[3] J. Paul Chen and L. L. Lim, "Recovery of precious metals by an electrochemical deposition method," *Chemosphere*, vol. 60, no. 10, pp. 1384–1392, 2005.

[4] M. a. Barakat, "New trends in removing heavy metals from industrial wastewater," *Arab. J. Chem.*, vol. 4, no. 4, pp. 361–377, 2011.

[5] Y. bo Su, Q. biao Li, Y. peng Wang, H. tao Wang, J. le Huang, and X. Yang, "Electrochemical reclamation of silver from silver-plating wastewater using static cylinder electrodes and a pulsed electric field," *J. Hazard. Mater.*, vol. 170, no. 2–3, pp. 1164–1172, 2009.

[6] A. Liu, X. Ren, M. An, J. Zhang, P. Yang, B. Wang, Y. Zhu, and C. Wang, "A combined theoretical and experimental study for silver

electroplating," *Sci. Rep.*, vol. 4, p. 3837, 2014.

[7] Y. Gao, Y. Zhou, H. Wang, W. Lin, Y. Wang, D. Sun, J. Hong, and Q. Li, "Simultaneous silver recovery and cyanide removal from electroplating wastewater by pulse current electrolysis using static cylinder electrodes," *Ind. Eng. Chem. Res.*, vol. 52, no. 17, pp. 5871–5879, 2013.

[8] "ASTM B700-97(2002), Standard Specification for Electrodeposited Coatings of Silver for Engineering Use, ASTM International, West Conshohocken, PA, 2002, www.astm.org," 2002.

[9] B. Matisoff, *Handbook of Electronics Manufacturing Engineering*. Springer US, 2012.

[10] J. chun Lee and B. D. Pandey, "Bio-processing of solid wastes and secondary resources for metal extraction - A review," *Waste Manag.*, vol. 32, no. 1, pp. 3–18, 2012.

[11] S. W. Won, P. Kotte, W. Wei, A. Lim, and Y. S. Yun, "Biosorbents for recovery of precious metals," *Bioresour. Technol.*, vol. 160, pp. 203–212, 2014.

[12] N. Das, "Recovery of precious metals through biosorption - A review," *Hydrometallurgy*, vol. 103, no. 1–4, pp. 180–189, 2010.

[13] C. Mack, B. Wilhelmi, J. R. Duncan, and J. E. Burgess, "Biosorption of precious metals," *Biotechnol. Adv.*, vol. 25, no. 3, pp. 264–271, 2007.

[14] S. Menezes, G. G. Leita, A. S. Reis, C. Tereza, and L. L. Mensor, "Screening of Brazilian Plant Extracts for Antioxidant Activity by the Use of DPPH Free Radical Method," vol. 130, pp. 127–130, 2001.

[15] S. Iravani, "Green synthesis of metal nanoparticles using plants," *Green Chem.*, vol. 13, no. 10, pp. 2638–2650, 2011.

[16] N. A. N. Mohamad, N. A. Arham, J. Jai, and A. Hadi, "Plant Extract as Reducing Agent in Synthesis of Metallic Nanoparticles: A Review," *Adv. Mater. Res.*, vol. 832, pp. 350–355, 2014.

[17] N. A. Arham, N. A. N. Mohamad, J. Jai, J. Krishnan, and N. M. Yusof, "Application of Response Surface Methodology in Extraction of Bioactive Component from Palm Leaves (Elaeis guineensis)," *Int. J. Sci. Eng.*, vol. 5, no. 2, pp. 95–100, 2013.

[18] M. Komethi, N. Othman, H. Ismail, and S. Sasidharan, "Comparative study on natural antioxidant as an aging retardant for natural rubber vulcanizates," *J. Appl. Polym. Sci.*, vol. 124, no. 2, pp. 1490–1500, 2012.

[19] N. A. Ramli, J. Jai, and N. M. Yusof, "Green Synthesis of Silver Nanoparticles Using *Elaeis guineensis* (Palm Leaves): An Investigation on the Effect of Reaction Time in Reduction Mechanism and Particle Size," *Appl. Mech. Mater.*, vol. 575, pp. 36–40, 2014.

[20] V. V. Makarov, a. J. Love, O. V. Sinitsyna, S. S. Makarova, I. V.

Yaminsky, M. E. Taliansky, and N. O. Kalinina, "'Green' nanotechnologies: Synthesis of metal nanoparticles using plants," *Acta Naturae*, vol. 6, no. 20, pp. 35–44, 2014.

[21] R. Veerasamy, T. Z. Xin, S. Gunasagaran, T. F. W. Xiang, E. F. C. Yang, N. Jeyakumar, and S. A. Dhanaraj, "Biosynthesis of silver nanoparticles using mangosteen leaf extract and evaluation of their antimicrobial activities," *J. Saudi Chem. Soc.*, vol. 15, no. 2, pp. 113–120, 2011.

[22] N. A. Ramli, J. Jai, N. Mohd Yusof, and N. A. Zamanhuri, "Green Synthesis of Silver Nanoparticles Using Elaeis Guineensis from Palm Leaves: Influence of pH in Reaction Kinetic," in *Advanced Materials Research*, 2015, vol. 1113, pp. 560–565.

[23] S. Kalidhasan, M. Ganesh, S. Sricharan, and N. Rajesh, "Extractive separation and determination of chromium in tannery effluents and electroplating waste water using tribenzylamine as the extractant," *J. Hazard. Mater.*, vol. 165, no. 1–3, pp. 886–892, 2009.

[24] N. M. Zain, A. G. F. Stapley, and G. Shama, "Green synthesis of silver and copper nanoparticles using ascorbic acid and chitosan for antimicrobial applications," *Carbohydr. Polym.*, vol. 112, pp. 195–202, 2014.

[25] T. K. Sau and A. L. Rogach, "Nonspherical noble metal nanoparticles: colloid-chemical synthesis and morphology control," *Adv. Mater.*, vol. 22, no. 16, pp. 1781–1804, 2010.

[26] J. A. Dean and N. A. Lange, *Lange's Handbook of Chemistry*, no. Bd. 15. McGraw-Hill, 1999.

[27] U. B. Jagtap and V. A. Bapat, "Green synthesis of silver nanoparticles using Artocarpus heterophyllus Lam. seed extract and its antibacterial activity," *Ind. Crops Prod.*, vol. 46, pp. 132–137, 2013.

[28] N. Agasti and N. K. Kaushik, "One Pot Synthesis of Crystalline Silver Nanoparticles," *Am. J. Nanomater.*, vol. 2, no. 1, pp. 4–7, 2014.

[29] S. Ashokkumar, S. Ravi, V. Kathiravan, and S. Velmurugan, "Synthesis, characterization and catalytic activity of silver nanoparticles using Tribulus terrestris leaf extract," *Spectrochim. Acta - Part A Mol. Biomol. Spectrosc.*, vol. 121, pp. 88–93, 2014.